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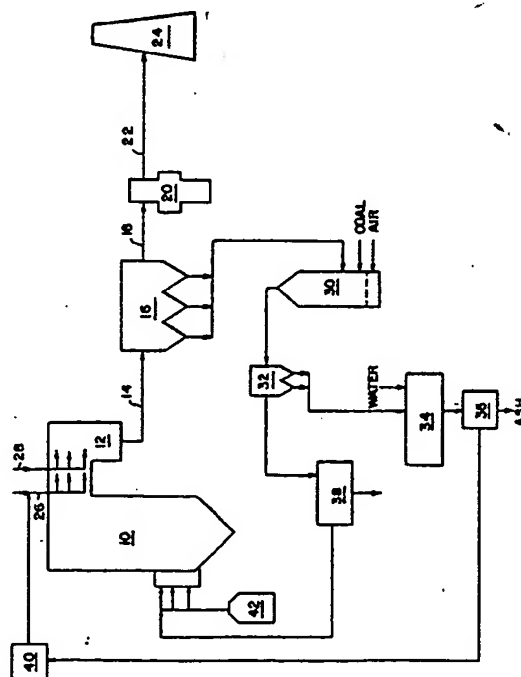
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Controlling emission of pollutants from coal-fired boiler systems.

In a method of controlling emission of SO_x , NO_x and particulates from a coal-fired boiler system, that includes a boiler (10), an economiser (12) and a fabric filter baghouse (16), a reagent/catalyst in powdered form is added (26) into the combustion flue gas stream intermediate the boiler (10) and economiser (12) at a temperature below the melting point of the powder. The reagent/catalyst and ammonia (added at 28) are reacted with the SO_x and NO_x while the flue gas passes through the economiser (12). Further reaction is achieved as the gas is passed through a filter cake which forms on filter bags in the baghouse (16).



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CONTROLLING EMISSION OF POLLUTANTS FROM COAL-FIRED BOILER SYSTEMS

This invention relates to controlling emission of pollutants from coal-fired boiler systems, for example in coal-fired electric power plants.

Advanced control technologies have rapidly evolved during the past two decades for dealing with emission from coal-fired power plants of particulates, sulphur oxides and nitrogen oxides.

A dramatic shift to low-sulphur coals, which produce high-resistivity fly-ashes, that are more difficult to collect, and the concurrent demand for increased particulate efficiency, has placed a heavy burden on conventional dust collectors (electrostatic precipitators) employed in these applications. Consequently, in the last 1970s the electric utility industry began, on a significant scale, to utilise alternative technology --fabric filterhouses-- for particulate control.

In a bag filterhouse (baghouse), fly-ash is separated from flue gas by filtration, i.e. the fly-ash is collected on the upstream side of tubularly shaped fabric filter bags as the gas is directed through the filter bags. The flue gas passes through a filter bag, typically from the inside out, and the fly-ash is collected as so-called filter cake. The material collected on the bag becomes part of the filtering medium. After a certain build-up of filter cake over the course of operation, the bags must be cleaned to avoid excessive pressure drop in order to maintain proper gas volume flow. The use of a bag filterhouse gives the utility company the option of switching coals since bag filterhouse collection efficiency is relatively insensitive to fuel characteristics.

Nevertheless, as coal burns, most of the sulphur content is converted to sulphur oxides (SO_x), typically SO_2 and SO_3 . In addition, oxides of nitrogen (collectively referred to as NO_x) are formed. Utilisation and placement of NO_x and SO_x control equipment upstream of the bag filterhouse will influence inlet conditions. Overall location of the bag filterhouse relative to such equipment, as well as the plant air heaters, flue gas temperature, flue gas composition, and fabric filter specifications including material properties such as composition, tensile strength, abrasion resistance, chemical resistance and temperature limitations, comprise the major parameters which must be carefully considered, integrated and controlled in order to achieve satisfactory overall plant emission control.

Our US Patent No. US-A-4 309 386 discloses a system in which a hot catalytic baghouse (greater than 316°C (600°F)) is used for simultaneous particulate removal and NO_x reduction. According to US-A-4 309 386, filter bags of the baghouse are treated with a catalyst to facilitate a selective cata-

lytic reduction process while simultaneously filtering out particulate matter from the gas stream. The baghouse is situated downstream from an ammonia injection system. In the baghouse, the flue gas stream is exposed to the treated bags to effect NO_x removal. However, that system has several potential shortcomings. In particular, bags impregnated with the catalyst tend to have a limited life span, necessitating periodic replacement of the entire bag, and the catalyst is subject to SO_x poisoning which can lead to loss of ability to reduce NO_x in the presence of gases containing high quantities of SO_x .

Therefore, continuing improvements are being sought in emission control systems employing fabric baghouses with satisfactory control of SO_x and NO_x emissions.

According to one aspect of the invention there is provided an integrated injection and baghouse system which collects and removes SO_x and particulates from a flue gas stream while reducing NO_x to harmless N_2 .

According to another aspect of the invention there is provided a method of controlling emission of pollutants from a coal-fired boiler system, which system includes a boiler, an economiser, a fabric filter baghouse and an air heater in a serial fluid communication path, by removing, in a temperature range of about 316°C to 427°C (600°F to 800°F), SO_x , NO_x and particulates from a combustion flue gas stream passing through said path, the method comprising the steps of:

(a) adding a reagent/catalyst in powdered form and ammonia into the combustion flue gas stream upstream of the fabric filter baghouse in a temperature zone having a temperature below the melting point of the reagent/catalyst;

(b) reacting some of the reagent/catalyst and ammonia with the SO_x and NO_x to form reaction products while passing the flue gas stream to the baghouse;

(c) separating the particulates, the reaction products and reagent/catalyst from the flue gas within the temperature range by filtration in the baghouse to form a filter cake;

(d) passing the flue gas stream through the filter cake to react additional reagent/catalyst and ammonia with the SO_x and NO_x to form additional reaction products and cleansed gas; and

(e) venting the cleansed gas out of the baghouse through the air heater.

According to a further aspect of the invention, a suitable reagent/catalyst, such as sodium aluminate, is pneumatically injected into a boiler in fine powder form, in a temperature zone below the

melting point of the reagent/catalyst, upstream of a hot baghouse, which is operating in a temperature range of 600°F to 800°F (approximately 316°C to 427°C) and which is located between an exit of an economiser of the boiler and an air heater. Ammonia is also injected in this vicinity. A reaction between the NO_x and ammonia converts the NO_x to harmless nitrogen gas and a reaction between SO_x and the reagent produces a solid particulate which continues to flow with the flue gas. The mixture of reactants, reaction products, and flue gases continues to flow to the baghouse, where the particulates are separated from the flue gas.

The injection technique advantageously provides an extended time for reaction of the reagent/catalyst and the SO_x and NO_x as the flue gas stream flows from the injection point to fabric filter bags of the baghouse. Further reaction takes place as the solids are collected in the filter bags as filter cake and the flue gases continue to pass through the filter cake.

In accordance with a preferred feature of the invention, the reagent/catalyst is removed from the baghouse, along with the fly-ash, for regeneration. Poisoning of the catalyst with SO_x is no longer a problem since the method seeks to achieve reaction of the reagent/catalyst with SO_x to remove the sulphur oxides from the gas stream and the reaction is otherwise acceptable due to the continuous replenishment of the reagent/catalyst by regeneration.

The invention will now be further described, by way of illustrative and non-limiting example, with reference to the accompanying drawing, the sole figure of which is simplified flow diagram illustrating a preferred arrangement for carrying out a method embodying the invention.

The drawing shows a coal-fired boiler 10 that includes an economiser 12 which is designed, as is well known, to remove heat from the combustion flue gases after the gases leave steam-generating and superheating sections of the boiler 10. An outlet of the economiser 12 is connected through a flue gas conduit 14 to a baghouse 16 in which particulates are collected in filter bags (not shown). The treated gas is discharged from the baghouse 16 through a conduit 18 to an air preheater 20 and then through a conduit 22 to a stack 24 for ultimate discharge to the atmosphere.

Injection lines 26, 28 are provided for injecting a solid reagent/catalyst and ammonia (NH₃), respectively, into a zone, having a temperature below the reagent/catalyst melting point, upstream of the baghouse 16. For example, as shown in the drawing, the solid reagent/catalyst and ammonia are injected upstream of the economiser 12, i.e. intermediate the boiler 10 and economiser.

Pneumatic injection of the reagent/catalyst, via

wall injectors, is preferred. The ammonia is preferably injected between a primary superheater and the economiser 12 as placement further upstream would result in excessive loss of ammonia by oxidation. The temperature at the economiser inlet will typically be between 371°C and 538°C (700°F and 1000°F), and the preferred operating range is 316°C to 427°C (600°F to 800°F). Reagents are selected which will not react with ammonia in this temperature range.

The combustion flue gas, which contains particulates, SO_x and NO_x, reacts with the reagent/catalyst as it flows through the economiser 12 and to the baghouse 16. As the gas flows from the injection point through the baghouse 16, the catalyst reacts with SO_x and NO_x and ammonia. The catalyst reacts further as it collects in the filter bags and the flue gas passes through it.

Sodium aluminate is the preferred reagent/catalyst. Other reagent/catalysts include transition metal oxides of titanium, vanadium, manganese, cobalt, iron, nickel, copper and zinc; alumina (particularly gamma phase) and alkalis alumina; alkali and alkaline earth oxides and carbonates; and minerals such as dawsonite, analcite, magnesioriebeckite, feldspars, alunite, anatase, azurite, bauxite, bunsenite, gothite, hematite, iron spinel, ilmenite, malachite, manganite, manganosite, mellite, siderite, and spinel.

The spent reagent/catalyst material is removed from the baghouse 16 with the fly-ash. The spent material contains sulphur from the flue gas in the form of sulphates and sulphites. The spent material and fly-ash are then fed into a fluid bed gasifier 30 where coal is added as a fuel source and the temperature of the sulphated spent material is raised to a level where the sulphur is driven off in the form of sulphur dioxide and hydrogen sulphide. The reagent/catalyst is then removed from the gas stream with the fly-ash via a particulate collector 32, such as a secondary baghouse, precipitator, or high efficiency cyclone. The collected solids are then added to water in a mixing tank 34 to form a slurry. The reagent/catalyst goes into solution. The slurry is then directed to a solid separator 36, such as a belt filter or centrifuge, where the ash is removed from the system. The solution containing the regenerated reagent/catalyst is then recycled as make-up back to the boiler 10. A drier 40 may be required prior to injecting the reagent/catalyst into the boiler.

The spent gas from the fluid bed gasifier 30 may be taken to a Claus plant 38 where the SO₂ and H₂S may be recovered in the form of elemental sulphur. A portion of the steam produced in the fluid bed gasifier 30 may be used for the operation of the Claus plant 38. The low Btu gas would then be sent back to the boiler 10 as additional fuel

with pulverised coal from a pulveriser 42 or could be used for other plant process requirements. There is a possibility that this gas could be used in the production of ammonia which in turn could be used as the make-up for the NO_x reduction process.

Claims

1. A method of controlling emission of pollutants from a coal-fired boiler system, which system includes a boiler (10), an economiser (12), a fabric filter baghouse (16) and an air heater (20) in a serial fluid communication path, by removing, in a temperature range of about 316°C to 427°C (600°F to 800°F), SO_x , NO_x and particulates from a combustion flue gas stream passing through said path, the method comprising the steps of:

(a) adding (26,28) a reagent/catalyst in powdered form and ammonia into the combustion flue gas stream upstream of the fabric filter baghouse (16) in a temperature zone having a temperature below the melting point of the reagent/catalyst;

(b) reacting some of the reagent/catalyst and ammonia with the SO_x and NO_x to form reaction products while passing the flue gas stream to the baghouse (16);

(c) separating the particulates, the reaction products and reagent/catalyst from the flue gas within the temperature range by filtration in the baghouse (16) to form a filter cake;

(d) passing the flue gas stream through the filter cake to react additional reagent/catalyst and ammonia with the SO_x and NO_x to form additional reaction products and cleansed gas; and

(e) venting the cleansed gas out of the baghouse (16) through the air heater (20).

2. A method according to claim 1, wherein the reagent/catalyst is sodium aluminate.

3. A method according to claim 1, wherein the reagent/catalyst is selected from metal oxides of titanium, vanadium, manganese, cobalt, iron, nickel, copper and zinc.

4. A method according to claim 1, wherein the reagent/catalyst is selected from alumina and alkali alumina.

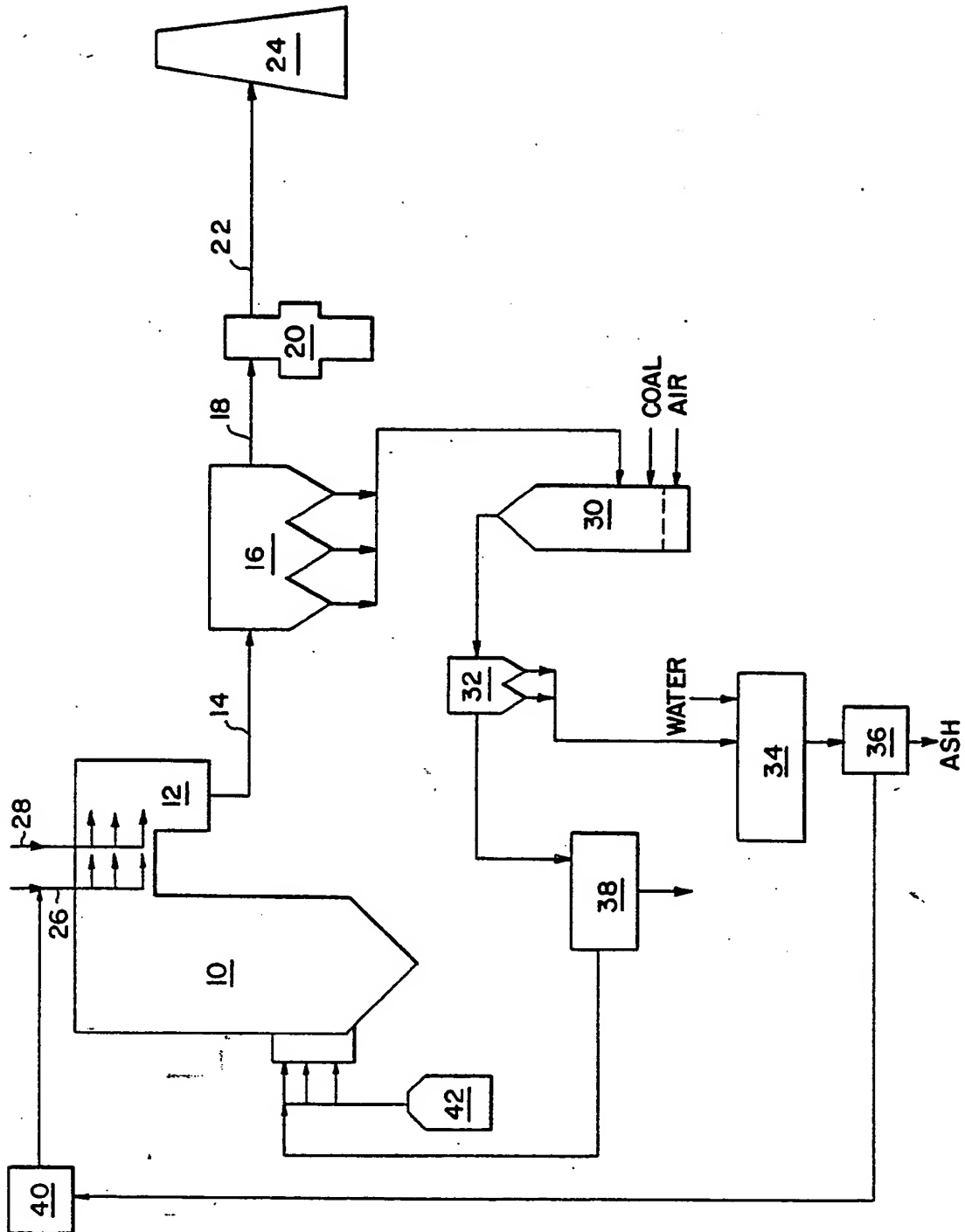
5. A method according to claim 1, wherein the reagent/catalyst is selected from alkali and alkaline earth oxides and carbonates.

6. A method according to claim 1, wherein the reagent/catalyst is selected from dawsonite, analcite, magnesioriebeckite, feldspar, alunite, anatase, azurite, bauxite, bunsenite, gothite, hematite, iron spinel, ilmenite, malachite, manganite, mannosite, mellite, siderite and spinel.

7. A method according to any one of the preceding claims, wherein the adding step (a) comprises adding the reagent/catalyst intermediate the boiler (19) and the economiser (12).

8. A method according to claim 7, wherein the reacting step (B) comprises reacting some of the reagent/catalyst and ammonia with the SO_x and NO_x to form reaction products while passing the flue gas stream through the economiser (12) to the baghouse (16).

9. A method according to any one of the preceding claims, comprising reclaiming reagent/catalyst from the cake by heating (30) the cake to a temperature sufficient to volatilise and drive off sulphur dioxide and hydrogen sulphide from the cake and form remaining solids containing recoverable reagent/catalyst, and separating (32) the recoverable reagent/catalyst from the solids, and wherein the adding step (a) includes passing the recovered reagent/catalyst into the combustion gas stream.





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 30 7884

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A,P	EP-A-0 217 733 (MITSUBISHI JUKOGYO K.K.) * claims 1-3 * ---	1,4,5	B 01 D 53/34
A	US-A-4 464 350 (M.L. KAPLAN) * claims 1, 3, 5-7 * ---	1,3	
A	DE-A-3 235 020 (H. HÖLTER) * claim 1; page 4, lines 12-16 * -----	1,5	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			B 01 D 53/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 12-01-1988	Examiner BERTRAM H E H
CATEGORY OF CITED DOCUMENTS			
<p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document</p>			

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(54) **Use of manganese compounds to inhibit both low- and high-temperature corrosion in utility and industrial furnace systems**

(57) The present invention relates to the reduction or inhibition of corrosion in an atmospheric burner unit by adding to a combustion system an effective amount of manganese, or a manganese precursor source, or derivative. The system may further include a catalyst package that may be composed of one or more individual organometallic compounds of Li, Na, K, Mg, Ca, Sr, Ba, Mo, Fe, Co, Pt, Ce, and combinations, mixtures or precursors thereof. The manganese component of the

catalyst package of the present invention reduces or eliminates the poisoning of the combustion system, whereby improved combustion and reduced emissions result. In addition, this invention inhibits both high- and low-temperature corrosion that occurs on the hot surfaces of burner furnace walls and tubes, and on cooler surfaces of the burner unit exhaust stack.

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Description**FIELD OF THE INVENTION**

5 [0001] The present invention relates to the reduction or inhibition of corrosion in an atmospheric burner unit by using a fuel-borne organometallic combustion system containing manganese, or a manganese precursor source, or derivative. The system may further contain a catalyst package that may be composed of one or more individual organometallic compounds of Li, Na, K, Mg, Ca, Sr, Ba, Mo, Fe, Co, Pt, Ce, and combinations, mixtures or precursors thereof. The
 10 manganese component of the catalyst package of the present invention reduces or eliminates the poisoning of the combustion system, whereby improved combustion and reduced emissions result. In addition, this invention serves a second purpose of lowering both high- and low-temperature corrosion that occurs on the hot surfaces of burner furnace walls and tubes, and on cooler surfaces of the burner unit exhaust stack.

BACKGROUND OF THE INVENTION

15 [0002] Fuel-borne organometallic combustion catalysts are becoming important in the control of environmental pollutants where fossil fuel is burned, for example, in internal combustion engines and in stationary burners such as those used in home heating, industrial furnaces, and steam power generators that burn fuel oil or coal. Organometallics derived from transition metals such as manganese, cerium, platinum, iron, and molybdenum; alkali metals such as
 20 lithium, sodium, and potassium; and alkaline earth metals such as calcium, magnesium, strontium and barium can all serve variously as effective fuel-borne emission control catalysts for controlling production of soot, smoke, hydrocarbon, carbon monoxide, sulfur trioxides, and oxides of nitrogen emissions. However, the vast majority of fossil fuels contain certain contaminant elements such as sulfur, phosphorus, vanadium, etc. that bind with these fuel-borne catalysts and inhibit them from efficiently performing their intended purpose. In addition, some combustion units are constructed with
 25 metals, such as iron, which can oxidize, corrode, or poison an emission control system.

[0003] High-temperature corrosion (above 400° C) occurring on hot surfaces of the combustion unit is promoted by fuel contaminants such as sodium, vanadium and iron. This corrosion is promoted by oxygen near and on the surfaces in question. Sodium vanadate combustion products absorb this oxygen to form low-melting sodium vanadylvanadate
 30 fluxes that oxidatively corrode and physically erode the metal surface by forming a corrosive and free-flowing surface alloy with the metal. Fuels such as coal that have high levels of iron give an ash surface deposit whose fusion temperature falls with iron concentration increase in the fuel. The iron in effect lowers the fusion temperature of the slag, and just like the low melting sodium vanadylvanadate fluxes described above, this molten slag corrodes and erodes the metal surface in a similar manner.

[0004] Low-temperature corrosion (below 250° C) can occur in the cooler region of a combustion unit towards the
 35 exhaust stack. Fuel sulfur, sodium, vanadium and iron can cause this corrosion. Sodium vanadylvanadates and iron, in the presence of oxygen, both independently catalyze conversion of SO₂ to SO₃ at high temperatures and the resulting SO₃ hydrates with combustion water at lower temperatures in the exhaust stack to give corrosive sulfuric acid. The key to both high- and low-temperature corrosion processes is availability of oxygen near species and surfaces capable of shunting it into the corroding surfaces. To avoid an expensive maintenance cost, corrosion must be inhibited or
 40 slowed down. It would therefore be desirable to scavenge the oxygen used to promote the corrosion.

[0005] Fuel-borne organometallic combustion and emissions control catalysts, such as those of cerium, platinum, manganese, and iron are used in engines and burners both to lower exhaust particulates, NO_x, hydrocarbon, etc. and as light-off catalysts for passive diesel particulate filters (DPFs), catalyzed diesel particulate filters (C-DPFs), and continuously regenerating technology diesel particulate filters (CRT-DPFs) used to filter particulate from the exhaust
 45 stream. The true efficiency of these catalytic additives is compromised by the presence in the fuel, or from the surfaces of the combustion unit, of certain metal contaminants with which these additives have to react first. In doing so, a portion of the catalytic activity of the additive is sacrificed and is no longer available to perform its intended task.

SUMMARY OF THE INVENTION

50 [0006] According to the present invention, manganese, when introduced in its various forms preferentially reacts with the fuel contaminants or surface contaminants thus allowing the respective organometallic catalyst to complete its intended emission control role more efficiently.

[0007] By the present invention, the manganese also scavenges oxygen away from critical surfaces and from species
 55 such as sodium vanadylvanadates, iron, platinum, etc. that would otherwise utilize this oxygen to promote surface corrosion, and shunts this oxygen to the more desirable carbon oxidation reactions. The manganese in the catalyst package achieves this by reacting with this oxygen and using it to oxidize carbon, and carbon monoxide to carbon dioxide. The result is a significant reduction in corrosion of the surface areas of the combustion unit and its exhaust

passageways.

[0008] In one embodiment of the present invention, it has thus been discovered that manganese in the fuel when admixed with fuel-borne organometallic catalysts preferentially reacts with certain contaminants in the fuel or otherwise introduced into the combustion, such as sulfur, vanadium, iron and phosphorus. The interaction between manganese and the fuel contaminant produces a non-poisoning environment in which it is ideal for the organometallic catalysts to effectively operate. The catalysts useful in the present invention can include one or more organometallic compounds of elements selected from the group consisting of Li, Na, K, Mg, Ca, Sr, Ba, Mo, Fe, Co, Pt, Ce, and combinations, mixtures, or precursors thereof.

[0009] In another embodiment is provided a method to inhibit corrosion of a combustion unit combusting a fuel, whereby the method includes adding to the combustion a corrosion-inhibiting amount of a manganese source.

[0010] By "interaction," "interacting," "interact" and "interacts" herein is meant scavenging.

[0011] By "scavenging" herein is meant the contacting, combining with, reacting, incorporating, chemically bonding with or to, physically bonding with or to, adhering to, agglomerating with, affixing, inactivating, rendering inert, consuming, alloying, gathering, cleansing, consuming, or any other way or means whereby a first material makes a second material unavailable or less available.

[0012] By "manganese" herein is meant any manganese or manganese-containing material, compound or precursor, such as but not limited to methyl cyclopentadienyl manganese tricarbonyl, available from Ethyl Corporation as MMT®, and manganese sulfonate, manganese phenate, manganese salicylate, cyclopentadienyl manganese tricarbonyl, alkyl cyclopentadienyl manganese tricarbonyl, organic manganese tricarbonyl derivatives, alkyl cyclopentadienyl manganese derivatives, *bis*-cyclopentadienyl manganese, *bis*-alkyl cyclopentadienyl manganese, neutral and overbased manganese salicylates, neutral and overbased manganese phenates, neutral and overbased manganese sulfonates, manganese carboxylates, and combinations and mixtures thereof.

[0013] Thus, in an embodiment the present invention provides a method to inhibit corrosion of a combustion unit combusting a fuel, said method comprising adding to the combustion a corrosion-inhibiting amount of a manganese source.

[0014] Thus, in an another embodiment the present invention provides a fuel-borne organometallic combustion system, containing a fuel and a catalyst package containing at least one metal source, and manganese as a co-catalyst, wherein the manganese in the system combines or interacts with at least one fuel contaminant selected from the group consisting of sulfur, phosphorus, vanadium, iron, and compounds thereof, and precursors thereof.

[0015] The contaminant, such as sulfur, vanadium, iron, phosphorus, and other elements and their precursors, can originate in or from the degradation of the steel or iron-containing structural units of the combustion unit and/or its exhaust passageways. The contaminant can also find its way into the combustion system of the present invention by or from any other means or sources, such as but not limited to combustion aids and adjuvants, lubricants, in the fuel source, such as is often found in crude fuel, tar sands, coal or still bottoms, and air.

[0016] By "combustion unit" herein is meant any and all internal and external combustion devices, machines, boilers, furnaces, incinerators, evaporative burners, plasma burner systems, plasma arc, stationary burners and the like which can combust or in which can be combusted a hydrocarbonaceous fuel. The combustion units effective in the utilization of the present invention include any and all burners or combustion devices, including for example and without limitation herein, stationary burners, waste incinerators, diesel fuel burners, gasoline fuel burners, power plant generators, power plant furnaces, and the like. The hydrocarbonaceous fuel combustion units that may benefit from the present invention include all combustion units, systems, devices, and/or engines that burn or oxidatively decompose hydrocarbonaceous fuels.

[0017] Fuels suitable for use in the operation of combustion units of the present invention include hydrocarbonaceous fuels such as but not limited to diesel fuel, jet fuel, alcohols, ethers, kerosene, low sulfur fuels, synthetic fuels, such as Fischer-Tropsch fuels, liquid petroleum gas, fuels derived from coal, coal, genetically engineered biofuels and crops and extracts therefrom, natural gas, propane, butane, unleaded motor and aviation gasolines, and so-called reformulated gasolines which typically contain both hydrocarbons of the gasoline boiling range and fuel-soluble oxygenated blending agents, such as alcohols, ethers and other suitable oxygen-containing organic compounds. Other fuels that are useful in the methods and combustion units of the present invention are gasoline, bunker fuel, coal (dust or slurry), crude oil, refinery "bottoms" and by-products, crude oil extracts, hazardous wastes, yard trimmings and waste, wood chips and saw dust, agricultural waste, fodder, silage, plastics and other organic waste and/or by-products, and mixtures thereof, and emulsions, suspensions, and dispersions thereof in water, alcohol, or other carrier fluids. By "diesel fuel" herein is meant one or more fuels selected from the group consisting of diesel fuel, biodiesel, biodiesel-derived fuel, synthetic diesel and mixtures thereof.

[0018] Oxygenates suitable for optional use in the present invention include methanol, ethanol, isopropanol, *t*-butanol, mixed alcohols, dimethoxy ethane (DME), methyl tertiary butyl ether, tertiary amyl methyl ether, ethyl tertiary butyl ether and mixed ethers. Oxygenates, when used, will normally be present in the reformulated gasoline fuel in an amount below about 25% by volume, and preferably in an amount that provides an oxygen content in the overall fuel in the

range of about 0.5 to about 5 percent by volume.

[0019] Thus, in an embodiment the present invention provides a method to inhibit corrosion at a temperature less than 250 °C in the exhaust passageway of a combustion unit combusting a fuel, said method comprising adding to the combustion a corrosion-inhibiting amount of manganese.

5 [0020] Another feature of the present invention is to provide lower maintenance time, materials, and costs due to reduced low and high temperature corrosion occurring in the burner or combustion units. Thus is provided a method to reduce corrosion in the combustion unit and/or its exhaust passageway which contains steel, iron or other corrosion-prone materials in a combustion unit combusting fuel and a manganese source.

10 [0021] A further feature of the present invention is to provide a method of tying up elements, such as vanadium, iron, sulfur, and phosphorus, which can otherwise poison the catalytic activity of a catalysed fuel combustion system.

[0022] Accordingly, the present invention relates in another embodiment to use in a fuel-borne organometallic emissions control catalyst system of manganese as a co-catalyst, whereby the organometallic catalyst is rendered more effective to improve carbon burnout in either the combustion chamber or the exhaust stream, or both, where the temperature is above about 250 °C.

15 [0023] The present invention also relates in another embodiment to use in a fuel-borne organometallic emissions control catalyst system of manganese as a co-catalyst, whereby the organometallic catalyst is rendered more effective to control corrosive sulfur trioxide production in either the combustion chamber or the exhaust stream, or both, where the temperature is above about 250 °C.

20 [0024] Additionally, the present invention provides a combustion system having a fuel-borne organometallic emissions control combustion catalyst, wherein a fuel contaminant preferentially reacts with a manganese co-catalyst rather than the organometallic catalyst. In this manner, scavenging of the contaminant by the manganese is achieved.

[0025] In yet another embodiment, the present invention provides a method to passivate metal surfaces containing Fe_2O_3 within a combustion unit combusting a fuel, wherein the surfaces are exposed to the product of the combustion, and the method includes adding a sufficient amount of a source of manganese to the combustion, whereby the manganese reduces at least some of the Fe_2O_3 to Fe_3O_4 , whereby the metal surface is passivated.

25 [0026] The present invention further relates to methods to retard, impede or prevent the oxidation of SO_2 to SO_3 , since SO_3 is an undesirable combustion by-product. According to one embodiment of the present invention, the use of manganese in the combustion process or immediately thereafter prevents the undesired oxidation of SO_2 to SO_3 , usually catalysed by iron, platinum, and/or vanadium often found in combustion products. This has the beneficial effect of reducing or eliminating the production of acid rain-causing SO_3 from the combustion of hydrocarbonaceous fuel.

30 [0027] Thus, in yet another embodiment of the present invention is provided a method of improving the efficiency of fuel-borne organometallic combustion catalysts utilized in a fuel combustion system, comprising adding to a fuel having one or more contaminants selected from sulfur, vanadium, iron and phosphorus an amount of manganese sufficient to, upon combustion of the fuel, interact with at least one of the contaminants.

35 [0028] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention, as claimed.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

40 [0029] Thus, according to one embodiment of the present invention, the manganese can be added to the main catalyst package as a co-catalyst. The main catalyst package may be composed of one or more individual organometallic compounds of Li, Na, K, Mg, Ca, Sr, Ba, Mo, Fe, Co, Pt, Ce, and combinations or mixtures, or precursors thereof. The intended purpose of the catalyst is environmental pollution control by promoting carbon burnout in combustion particulate byproducts such as soot and smoke (particulate matter or PM), and in some instances control of hydrocarbon (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x) emissions. To the fuel treated with this catalyst package

45 can be added, for example and without limitation, between 2 - 18 mg Mn/liter fuel when used in internal combustion engines, and between 2 - 200 ppm v/v Mn/liter fuel when used in atmospheric burners such as those found in industrial furnaces, home heating, and utility power generation furnaces.

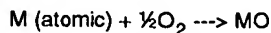
50 [0030] According to one embodiment of the present invention, a preferred manganese source is methylcyclopentadienyl manganese tricarbonyl, available from Ethyl Corporation as MMT® Gasoline Additive, or HITEC® 3000 Performance Additive, or GREENBURN® Fuel Additive.

[0031] In internal combustion engines, manganese in a fuel combines with, reacts with, inactivates or otherwise ties up catalysts poisons, such as sulfur and phosphorus, hence leaving a cleaner or clean combustion environment in which the fuel-borne organometallic catalyst can function with surprisingly improved efficiency.

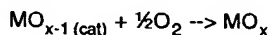
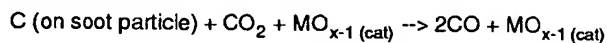
Carbon / Hydrocarbon Burnout and Carbon Monoxide Removal

55 [0032] Most organometallic-containing fuel additives decompose in the flame to give the respective metal atoms.

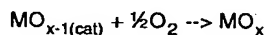
The level of fuel air mixedness at the time of combustion is nonhomogeneous because ignition occurs while the fuel is being injected and combustion heat radiates back into the fuel core as it is being injected, causing pyrolysis reactions of the fuel in this fuel-rich zone. The pyrolysis products form soot nucleation sites that grow into visible soot by coagulation and agglomeration mechanisms. As combustion takes place, manganese atoms from the thermal decomposition of the manganese-containing fuel additive collide with one another and with the fuel pyrolysis products, which are coagulating and agglomerating into visible soot. The metal atoms also collide with oxygen according to the schematic reaction below.



[0033] Any collisions between metal atoms (i.e. Pt, Fe, Ce, Mn, etc) in the combusting environment are non elastic (this is the nature of "naked" metal atom collisions) and lead to reduced dispersion of the metal in the combusting gases. However, collisions of metal atoms with fuel pyrolysis products as they agglomerate maintains the dispersion by charging the particles, resulting in soot particles that are impacted with highly dispersed metal atoms and with clusters thereof that might have formed prior to collision with soot particles. As this process transpires, the level of mixedness increases, and at temperatures above 400 °C thermal oxidation of the soot occurs as fast as oxygen collides with these particles. The rate of this oxidation is temperature dependent, slowing down as the temperature fall below 400 °C. However, particles with metal atoms impacted continue to oxidize at a high rate due to carbon oxidation catalyzed by carbon dioxide and the metal catalyst species as shown in the following equations.



[0034] This "carbon burnout" reaction catalyzed by metal oxides according to the above three equations can be sustained to temperatures as low as 250 °C. Finally, the carbon monoxide thus formed is further oxidized to carbon dioxide as oxygen abundance increases in the combusting mixture due to increasing level of mixing with time. This builds up the level of MO_x according to the reaction equations,



[0035] The reaction cycle above is oxygen concentration dependent and will continue to take place in the combustion gases all the way to temperatures as low as 250 °C. These carbon burnout, hydrocarbon oxidation and carbon dioxide removal reactions catalyzed by fuel borne organometallic catalysts such as compounds derived from Pt, Fe, Ce, etc. can be inhibited by fuel components bearing sulfur, phosphorus, vanadium, lead, etc. which react with and deactivate these catalysts.

[0036] By the present invention, a manganese compound can be added to the main catalyst package as a co-catalyst to scavenge these "poisons" from the combustion environment thus optimizing the performance of the main fuel-borne organometallic catalyst in promoting carbon burnout in combustion particulate byproducts.

[0037] In another embodiment, the manganese compound is not added to the main catalyst package directly, but is subsequently and/or separately introduced to the combustion unit or combustion byproducts therefrom.

[0038] In stationary burners the manganese in addition to combining with, reacting with, inactivating, or otherwise tying down sulfur and phosphorus, also inhibits SO_2 to SO_3 oxidation generally facilitated by Fe or Pt. The SO_3 hydrates in the exhaust stream as the temperatures drop below the dew point to give sulfuric acid that results in serious tail end corrosion in the exhaust stack. This so-called "low temperature corrosion" is minimized herein by the addition of a sufficient amount of a source of Mn in cases where the fuel-borne catalysts (i.e. Fe and Pt) or surface contaminants (e.g. Fe and oxides thereof) are known to also catalyze the SO_2 to SO_3 reaction.

[0039] Stationary burner furnaces also suffer from high temperature corrosion that is mainly caused by high iron and

vanadium levels in the fuel that form low melting iron derivatives, and vanadylvanadate fluxes with alkali and alkaline earth metals that may be added as fuel-borne combustion and emissions catalysts. Co-addition of manganese inhibits formation of low-melting alkali/alkaline earth metal vanadylvanadates by reacting with the oxygen necessary for the formation of these low melting fluxes. These fluxes corrode surfaces in the high temperature zone of stationary burner furnaces leading to frequent expensive maintenance work. An increase in vanadium and iron in the fly ash is a diagnosis of this high temperature corrosion. When manganese is added to the fuel according to the present invention, there is a decrease in these elements in the fly ash thereby indicating a decreased level of high temperature corrosion.

Optimization of catalytic activity and prevention of low-temperature corrosion.

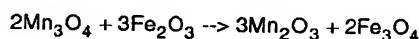
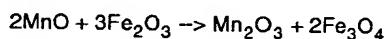
[0040] Sulfur trioxide (SO₃) produced in the combustion of hydrocarbonaceous fuels combines with water vapor to form sulfuric acid as the temperature of the exhaust cools down below the dew point of water. The presence of this acid results in both low temperature corrosion of exhaust equipment and in corrosive environmental pollution (acid rain). In atmospheric (stationary) burners, the corrosion of exhaust equipment can be quite considerable in terms of cost and down time for repairs. Fuel-borne metallic catalysts convert sulfur dioxide (SO₂) to sulfur trioxide at very high rates. The efficiencies of some of these reactions are shown below.

Surface metal catalyzed heterogeneous reactions of SO₂ to SO₃ have been summarized by Salooja as follows.

Reaction	Conversion Efficiency
$\text{SO}_2 + \frac{1}{2}\text{O}_2 (\text{Pt}_{\text{cat}}) \rightarrow \text{SO}_3 + (\text{Pt}_{\text{cat}})$	100%
$\text{SO}_2 + \frac{1}{2}\text{O}_2 (\text{V}_2\text{O}_{5\text{cat}}) \rightarrow \text{SO}_3 + (\text{V}_2\text{O}_{5\text{cat}})$	85%
$\text{SO}_2 + \frac{1}{2}\text{O}_2 (\text{Cr}_2\text{O}_{3\text{cat}}) \rightarrow \text{SO}_3 + (\text{Cr}_2\text{O}_{3\text{cat}})$	80%
$\text{SO}_2 + \frac{1}{2}\text{O}_2 (\text{Fe}_2\text{O}_{3\text{cat}}) \rightarrow \text{SO}_3 + (\text{Fe}_2\text{O}_{3\text{cat}})$	65%
$\text{SO}_2 + \frac{1}{2}\text{O}_2 (\text{CuO}_{\text{cat}}) \rightarrow \text{SO}_3 + (\text{CuO}_{\text{cat}})$	58%

The conversion efficiencies shown are achieved at temperatures of: 450 °C (Pt), 520 °C (V₂O₅), 575 °C (Cr₂O₃), 620 °C (Fe₂O₃), and 680 °C (CuO). (Salooja, K. C., Burner Fuel Additives, Journal of the Institute of Fuel, 37, p. 37, 1972.)

[0041] Platinum thus provides extremely efficient conversion of SO₂ to SO₃. This metal is used commercially at very low treat levels (2-4 ppm) in diesel as a fuel-borne catalyst for control of particulate and NO_x emissions. When it reacts with SO₂ to form undesirable SO₃, the reaction goes further to form PtSO₄ which is inactive towards its intended PM and NO_x control. When this fuel-borne catalyst is formulated with a manganese co-catalyst according to the present invention, the manganese will keep the sulfur away from the platinum by forming a sacrificial MnSO₄, thus maintaining the performance of the platinum at its optimum. In the case of iron, the active form in converting SO₂ to SO₃ is Fe₂O₃. The manganese used in this invention inhibits this reaction by reducing this active iron species to the less sulfur active Fe₃O₄ lower oxidation state form as shown below.



Fe₃O₄ does not promote the oxidation of SO₂ to SO₃. Since Fe₂O₃ but not Fe₃O₄ catalyzes thermal oxidation of SO₂ to SO₃, surface catalysis of SO₂ to SO₃ is eliminated or inhibited by the use of Mn in the present invention. And SO₃ formed by other reaction means within the combustion unit will react with MnO according to the reaction described by Gray below.



(Gray, M.A., "The Effect of a Volatile Fireside Manganese Additive on Coal-Fired Utility Boiler Operation," ASME presentation at the Joint Power Generation Conference, Phoenix, Arizona, Sept. 28 to Oct. 2, 1980).

[0042] Thus, the present invention provides in one embodiment a method to passivate metal structural surfaces within combustion units, which surfaces might otherwise catalyze the oxidation of SO₂ to SO₃. This passivation of iron and steel surfaces by manganese against catalyzing the SO₂ to SO₃ oxidation reaction is important in utility steam

furnaces where the surface area presented to the combustion products is by design very large in order to extract maximum heat from the flue gases to generate steam.

[0043] In another embodiment, the present invention prevents or inhibits the oxidation of Fe_3O_4 to Fe_2O_3 on a surface of a combustion unit. A manganese co-catalyst added with the fuel-borne catalyst according to an embodiment of the present invention maximizes the protective effect by ensuring the highest probability of the manganese being juxtaposed to the fuel-borne catalyst during the combustion and exhaust phases. Other fuel-borne catalyst poisons such as phosphorus, vanadium, etc. would be similarly inhibited or scavenged by the manganese.

High Temperature Corrosion

[0044] One skilled in the art can expect high temperature corrosion to occur if the fuel used contains sodium (Na), and/or vanadium (V), since highly corrosive complex oxides of these species such as " $5\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 11\text{V}_2\text{O}_5$ " (sodium vanadylvanadates) form on utility furnace surfaces in the temperature range between 550 and 680 °C. These low melting oxides are efficient as 1) SO_2 to SO_3 conversion catalysts, and 2) oxygen transport catalysts from the gas phase to the iron surface of the unit. A manganese co-catalyst added with the fuel-borne catalyst (Pt, Fe, Ce, etc.) would preferentially scavenge the oxygen from the surface deposit and utilize it in the carbon burnout reactions. This would inhibit oxidation of higher melting sodium vanadylvanadates to their more corrosive lower melting analogues which are responsible for high temperature corrosion by forming a eutectic flux with the utility furnace and pipes surfaces resulting in surface erosion. (See, for example, Pollman, S., Mineralogisch kristallographische Untersuchungen an Schlacken und Rohrbelägen aus dem Hochtemperaturbereich ölgefeuerter Großkessel. VGB-Mitteilungen, 94, p. 1, 1965. Volker Hoenig, L., "Untersuchung der Wirkungsmechanismen von Additiven für shweres Heizöl". Fortschritt-Berichte VDI, Reihe 15. Umwelttechnik, Nr. 84, pp. 57-59 and references therein, Düsseldorf. VDI-Verlag 1991, and Wahnschaffe, E., Kontinuierliche SO_3 - und Taubereichsmessung auf ölgefeuerten Dampferzeugern. Mitteilungen der VGB, Heft 3, p. 193, 1968.)

[0045] The following examples further illustrate aspects of the present invention but do not limit the present invention.

EXAMPLES:

[0046] When fuel-borne organometallic combustion control catalysts including a manganese source were utilized in a power plant generator burning #6 fuel oil according to an embodiment of the present invention, emission filters showed declining particulate mass with time. Specifically, a reduction in electrostatic precipitator ash as carbon of up to and including 38% by mass was observed.

[0047] Another measure of the effectiveness of reduced ash production is the observed trend of increasing efficiency such as resistivity as loss on ignition of an electrostatic precipitator fly ash decreases. This is because the carbon deposits act as a conductor on the electrostatic precipitator and resistivity is increased as carbon deposition and deposits are decreased. The overall efficiency of the combustion unit is increased according to the present invention by burning more particulate hence reducing the deposition of carbon ash.

[0048] The present invention is particularly effective in reducing the amount of vanadium and iron in the fly ash resulting from the combustion of fuel oil, such as for example #6 fuel oil, in a power plant furnace.

[0049] The present invention is particularly effective in lowering high- and low-temperature corrosion in steam utility power generator furnaces combusting a fuel oil as demonstrated by the modified composition of the fly ash and bottom ash shown in Figures 1 & 2. High temperature corrosion from the combustion of fuel oils loads these ashes with iron, sulfur, and vanadium. The iron comes from surface corrosion in the furnace and steam pipes surfaces.

[0050] Figure 1 shows a decrease in fly ash iron content as duration of manganese use increases from the combustion of #6 fuel oil according to the present invention. The sulfur level in the ash is also lowered showing that the manganese is inhibiting oxidation of SO_2 to SO_3 and the SO_3 would form either metallic sulfates on reaction with other fuel-borne and system surface metals, or form sulfuric acid on reaction with combustion water leading to low temperature corrosion. A decreasing amount of iron in the ashes is indicative of a lowering in high temperature surface corrosion, and a decreasing ash sulfur level is indicative of less sulfuric acid formation in the flue gases.

[0051] Figure 2 supplements the results in Figure 1 by showing a corresponding decrease in vanadium and sulfur in the bottom ash resulting from the combustion of #6 fuel oil. These decreases in iron, sulfur, and vanadium in the ashes do not trend with the respective levels in the fuel oil used. The corresponding levels of sulfur and vanadium in the fuel oil used were actually trending up with time as shown in Figure 3, hence demonstrating even more the unexpected efficacy of manganese to control the fate of these contaminants in the combustion system according to the present invention.

[0052] Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

Claims

1. A method to inhibit corrosion of a combustion unit combusting a fuel, said method comprising adding to the combustion a corrosion-inhibiting amount of a manganese source.
2. The method of claim 1, wherein the corrosion is at a temperature above 400° C.
3. The method of claim 1, wherein the corrosion is at a temperature below 250° C.
4. A method of reducing the amount of vanadium in the fly ash resulting from the combustion of a fuel containing vanadium in a combustion unit, said method comprising adding to the fuel or its combustion products an amount of a source of manganese effective to combine with the vanadium or its combustion products, whereby the amount of vanadium in the resulting fly ash is reduced.
5. A method of reducing the amount of iron in the fly ash resulting from the combustion of fuel containing iron in a combustion unit, said method comprising adding to the fuel or its combustion products an amount of a source of manganese effective to combine with the iron or its combustion products, whereby the amount of iron in the resulting fly ash is reduced.
6. A method of reducing the amount of sulfur in the fly ash resulting from the combustion of fuel containing sulfur in a combustion unit, said method comprising adding to the fuel or its combustion products an amount of a source of manganese effective to combine with the sulfur or its combustion products, whereby the amount of sulfur in the resulting fly ash is reduced.
7. A method for improving the effectiveness of one or more fuel-borne organometallic emissions control catalyst compounds of at least one element selected from the group consisting of Li, Na, K, Mg, Ca, Sr, Ba, Mo, Fe, Co, Pt, Ce, and combinations, mixtures, and precursors thereof for controlling sulfur trioxide production in or from the combustion in a combustion unit of a hydrocarbonaceous fuel having at least one contaminant selected from the group consisting of sulfur, vanadium, iron and phosphorus, said method comprising combining said at least one contaminant with a sufficient amount of manganese or a source thereof.
8. A method to passivate metal surfaces containing Fe_2O_3 within a combustion unit combusting a fuel, wherein said surfaces are exposed to the product of said combustion, said method comprising adding a sufficient amount of manganese or a source thereof to the combustion, whereby the manganese reduces at least some of the Fe_2O_3 to Fe_3O_4 , whereby the metal surface is passivated.
9. A method to inhibit the oxidation of Fe_3O_4 to Fe_2O_3 on a surface in a combustion unit combusting a fuel, said method comprising adding a sufficient amount of a source of manganese to the combustion, whereby manganese scavenges oxygen to thereby inhibit the oxidation of Fe_3O_4 to Fe_2O_3 .
10. A method of increasing the efficiency of an electrostatic precipitator of a combustion unit which combusts fuel and produces carbon-containing fly ash, said method comprising adding a sufficient amount of a source of manganese to the combustion, whereby carbon deposition on said electrostatic precipitator is decreased, and electrostatic precipitator efficiency is increased.
11. The method of any one of claims 1-10, wherein the combustion unit is selected from the group consisting of any and all burners or combustion units, stationary burners, waste incinerators, diesel fuel burners, gasoline fuel burners, power plant generators, power plant furnaces, any and all internal and external combustion devices, boilers, furnaces, evaporative burners, plasma burner systems, plasma arc, and devices that can combust or in which can be combusted a hydrocarbonaceous fuel.
12. The method of any one of claims 1-11, wherein the fuel is selected from the group consisting of diesel fuel, biodiesel, biodiesel-derived fuel, synthetic diesel, jet fuel, alcohols, ethers, kerosene, low sulfur fuels, synthetic fuels, Fischer-Tropsch fuels, liquid petroleum gas, fuels derived from coal, coal, genetically engineered biofuels and crops and extracts therefrom, natural gas, propane, butane, unleaded motor and aviation gasolines, reformulated gasolines which contain both hydrocarbons of the gasoline boiling range and fuel-soluble oxygenated blending agents, gasoline, bunker fuel, coal (dust or slurry), crude oil, refinery "bottoms" and by-products, crude oil extracts, hazardous wastes, yard trimmings and waste, wood chips and saw dust, agricultural waste, fodder, silage, plastics, organic

waste, and mixtures thereof, and emulsions, suspensions, and dispersions thereof in water, alcohol, and other carrier fluids.

- 5 13. A method of any one of claims 1-12, wherein the manganese is selected from the group consisting of methyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl manganese tricarbonyl, bis- cyclopentadienyl manganese (manganocene), bis- alkyl cyclopentadienyl manganese, manganese sulfonate, manganese phenate, manganese salicylate, alkyl cyclopentadienyl manganese tricarbonyl, organic manganese tricarbonyl derivatives, alkyl cyclopentadienyl manganese derivatives, neutral and overbased manganese salicylates, neutral and overbased manganese phenates, neutral and overbased manganese sulfonates, manganese carboxylates, and combinations and mixtures thereof.
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Figure 1

Fly Ash Elemental Composition: - Selected Elements

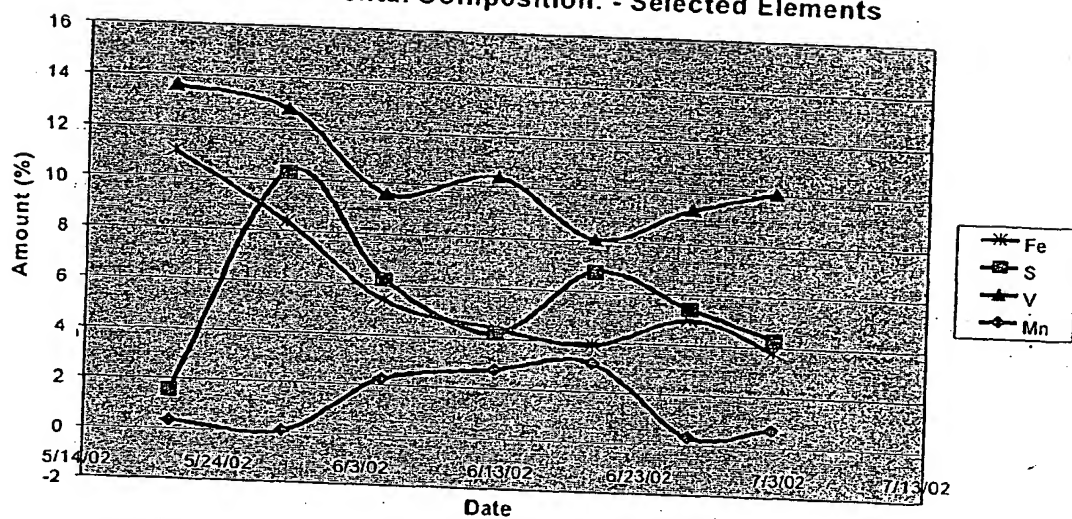
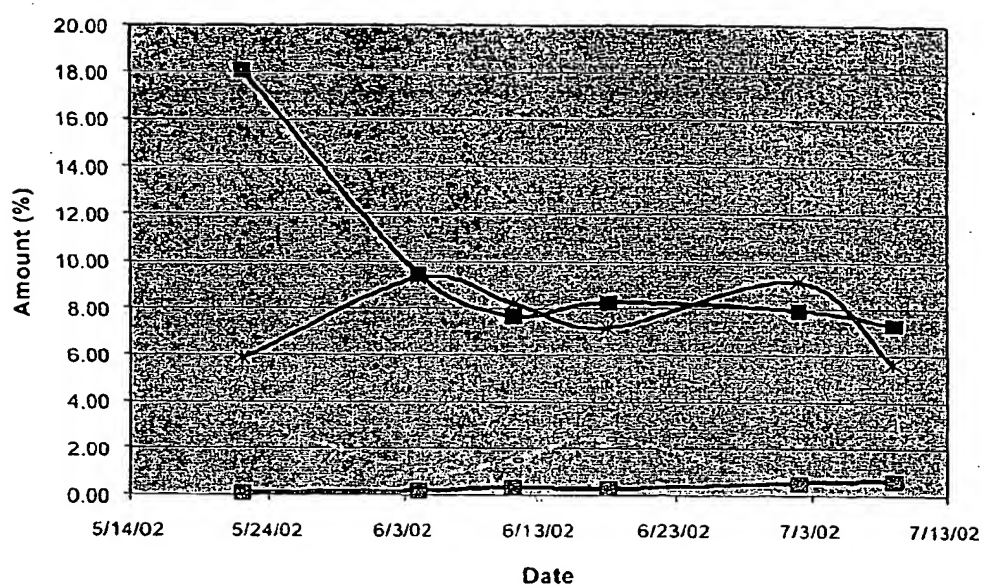


Figure 2

Bottom Ash Elemental Compositions: - Key Elements



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